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INSTRUCTIONS

FOR THE

ANALYSIS OF LIME AND CEMENT STONES,

AND OF

POTABLE WATERS.

BY

MURRAY THOMSON, M.D., F.R.S.E.,
FELLOW OF THE UNIVERSITY OF CALCUTTA AND PROFESSOR OF
EXPERIMENTAL SCIENCE IN THE THOMASON C. E. COLLEGE, ROORKEE.

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INSTRUCTIONS FOR THE ANALYSIS OF LIME AND CEMENT STONES.

SECTION I.

I. TESTS FOR THE RECOGNITION OF THE MORE COMMONLY OCCURRING CONSTITUENTS.

A.—*Tests for the Metals.*

ALUMINIUM = Al. Solutions of this metal show the following re-actions:—

1. *Potassic Hydrate*, KHO, in small amount produces a white gelatinous precipitate, $Al_2H_6O_6$. If KHO be now added in larger quantity, the gelatinous precipitate dissolves, and from this solution the $Al_2H_6O_6$ is reprecipitated by the addition of Ammonic Chloride NH_4Cl.

2. *Ammonic Hydrate*, NH_4HO, produces the same precipitate as potassic hydrate, but it is not soluble in excess of the re-agent.

IRON = Fe. Solutions of this Metal show two sets of re-actions, according as the metal exists in the solution in the form of the Ferrous or the Ferric Oxide.

FERROUS OXIDE, FeO. 1. Potassic Hydrate, KHO, a dirty-green precipitate, FeH_2O_2, not soluble in excess of KHO.

2. *Ammonic Hydrate* NH_4HO, produces the same precipitate as KHO.

3. *Potassic Ferrocyanide*, $K_4Fe(CN)_6$, a bluish-white precipitate, which deepens in colour by exposure to the air.

4. *Potassic Ferridcyanide*, $K_3Fe(CN)_6$: a deep-blue precipitate.

FERRIC OXIDE, Fe_2O_3. 1. *Potassic Hydrate:* a brownish-red precipitate, insoluble in excess of the re-agent. The same precipitate is given by Ammonic Hydrate.

2. *Potassic Ferrocyanide:* a deep blue precipitate (Prussian blue).

3. *Potassic Ferridcyanide:* a deep ruddy-green colour, but no precipitate.

4. *Ammonic Sulphocyanide:* a deep blood-red colour, but no precipitate.

CALCIUM = Ca. Solutions of this Metal give reactions as follow:—

1. *Ammonic Carbonate* $(NH_4)_2CO_3$: a white precipitate even in cold solutions.

2. *Ammonic Oxalate* $(NH_4)_2C_2O_4$: a white precipitate. This re-action occurs even when the solution is very dilute.

3. *Calcic Solutions* treated with alcohol, and the latter ignited, give a crimson red colour to the flame.

Magnesium = Mg. Solutions of this Metal give re-actions as follow:—

1. *Ammonic Carbonate* only precipitates Magnesic solutions on boiling.

2. *Ammonic Oxalate* gives a white precipitate, but only with much difficulty.

3. *Sodic Hydric Phosphate*, Na_2HPO_4, gives a scanty white precipitate. If the Magnesic solution be previously mixed with Ammonic Chloride and Ammonic Hydrate, then the Sodic Phosphate produces an abundant white crystalline precipitate. Even in dilute solution this latter re-action takes place.

Potassium. Solutions of this Metal give re-actions as follow:—

Platinic Tetrachloride, $PtCl_4$, in moderately concentrated, but not in dilute, solutions, a yellow crystalline precipitate. The precipitate comes quicker on stirring, and also by adding alcohol.

Tartaric Acid $C_4H_6O_6$, in moderately concentrated solutions, a white crystalline precipitate. The precipitation is promoted by stirring.

A potassium salt mixed with alcohol, and the alcohol ignited, the flame acquires a violet colour. If the potassium salt is held by a platinum wire in the inner part of the flame, the outer acquires the violet colour.

Sodium = Na. Solutions of this Metal are recognised by only one test, namely, the strong yellow colour t[illegible]ive to flame. This colour may be educed by either burning the sodium solution along with alcohol, or by moistening the loop of a platinum wire with the solution, and holding it in the inner part of a flame.

Ammonium = NH_4. Although this substance is not usually a constituent of Mortar or Cements, yet in connection with other parts of Engineering Chemistry, as for instance, testing of drinking waters, it is useful to know how it may be recognised. Uncombined, or free Ammonia, NH_4HO, has a strong pungent characteristic odour, but in combination this odour is not perceived. From its combinations, however, the Ammonia can be readily made free, as by treating them with potass, KHO, or slaked lime CaH_2O_2, when the odour is usually perceived.

Platinum Tetrachloride gives in moderately concentrated solutions a yellow precipitate.

Nessler test. This is an extremely delicate test for Ammonia, either free or in combination. The test solution is made by dissolving 35 parts of Potassic Iodide and 13 of Mercuric Chloride in 500 parts boiling water: a yellowish solution is thus obtained. To this is now added, by slow degrees, a cold saturated solution of Mercuric Chloride, until the red precipitate produced will not re-dissolve. To this is now added

test solution. It is made more sensitive still by the addition of a drop or two of saturated solution of Mercuric Chloride, and allowing the precipitate produced to subside.

This *Nessler solution*, when dropped into another solution containing the merest trace of any ammonia or ammoniacal salt, will produce a yellow colour or precipitate. If the amount of ammonic salt is large, a red-brown precipitate is freely produced.

B.—*Tests for the Acids.*

An acid may be defined to be the hydrogen compound, of an elementary, or compound radical, of the electro-negative kind, *i. e.*, opposed to hydrogen itself, or the metals, most of which are held to be electro-positive radicals: the hydrogen in the acid may be replaced by a metal, and then what is usually called a salt is produced. An acid generally has a sour taste, and turns a vegetable blue colour, like that of litmus, into red.

Carbonic Acid $= H_2CO_3$. This acid is very easily recognised, as it is easily displaced from its compounds by a stronger acid. When thus displaced, it escapes by effervescence as a colorless, odourless gas, a little heavier than air. When a little of the gas is allowed to fall into clear lime water, CaH_2O_2, the latter becomes muddy. If any lime or cement stone ground into rough shows the escape of this gas, then carbonic acid has certainly been present in it.

Sulphuric Acid = H_2SO_4. Solutions containing this acid give an abundant white precipitate with Baric Chloride $BaCl_2$, or Baric Nitrate $Ba(No_3)_2$. This white precipitate, $BaSO_4$, is insoluble in hydrochloric acid. This test, as now described, is quite enough to distinguish Sulphuric Acid.

Hydrochloric Acid = HCl. Not often a constituent of lime or cement stones.

1. A solution containing HCl gives a white curdy precipitate with Argentic Nitrate, $AgNO_3$, insoluble in Nitric Acid, HNO_3.

2. A solution containing hydrochloric acid, or more correctly stated, a solution containing a chloride treated with Manganic Binoxide, MnO_2, and Sulphuric Acid, and gently heated, evolves chlorine gas, which has a yellow colour, and very irritating odour. The occurrence of this colour and odour is enough to distinguish the presence of hydrochloric acid.

II. QUALITATIVE ANALYSIS OF A LIME OR CEMENT STONE.

A.—Detection of the Metals.

The stone is reduced to powder in an iron mortar, or if wanted very fine, in an agate mortar. For the detection of the aluminium, iron, calcium and magnesium, a portion of the powder is dissolved in dilute hydrochloric acid: the occurrence of effervescence at this stage, along with the characters of the escaping gas, will show the presence of carbonic acid.

In almost all cases, the hydrochloric acid will fail to dissolve the whole of the stone: what remains insoluble is clay, or a mixture of clay and sand. This residue is not further analysed, unless a very complete analysis is desired. According to the amount of this residue, the general character of the limestone may be determined: thus, if very small, the stone on burning will yield *rich* or *fat* lime, and as the quantity increases the *poorer* will be the lime which the stone will yield.

The soluble and insoluble parts are now separated by filtration.

The insoluble portion is washed in water by decantation several times, so as to separate the lighter clay from the heavier sand. The existence, or non-existence of both of these in the stone, may thus be proved.

The soluble portion has now added to it a little

Ammonic Chloride and Ammonic Hydrate: this last is added until the liquid smells of it. A whitey-brown precipitate is the usual result: this is now separated by filtration, and the filtrate is reserved for treatment as para. 4 directs.

2. The precipitate on the filter is now dissolved by having a very little warm dilute hydrochloric acid poured over it. The resulting solution has now added to it Sodic or Potassic Hydrate in excess. This mixture is well shaken, warmed, and filtered. The filtrate will contain the aluminium, if it is contained in the stone: to confirm its presence, add Ammonic Chloride; if a white flocculent precipitate occur, aluminium is certainly present.

3. The portion left on the filter from the last operation is again dissolved by dilute hydrochloric acid, and the presence of iron confirmed by one or more of its tests. To ascertain whether the iron is present in the form of ferrous or ferric oxides, or both, recourse is now had to a solution of the stone in cold dilute hydrochloric acid. A small quantity of the powdered stone is shaken up with the dilute acid, and when effervescence has finished, it is filtered, and to this solution the appropriate tests for ferrous and ferric oxides are applied.

4. The filtrate, directed to be reserved at end of para. 1, is now boiled, and while boiling, Ammonic Oxalate is added: the white abundant precipitate produced, is allowed to subside, and more Ammonic

Oxalate is added to the clear supernatant liquid. If no more precipitation occurs, then all the calcium has already separated in the precipitate, but if a further precipitate occurs, then more Ammonic Oxalate is added, so as to throw down the whole of the calcium. Generally, however, a liberal use of the Ammonic Oxalate in the first instance, secures the full precipitation of the calcium.

5. The white precipitate of Calcic Oxalate is now separated by a filter. The filtrate contains Magnesium, and its presence may be confirmed by the hydric sodic phosphate test.

6. Proceed now to prove the presence of Potassium or Sodium, or both. These metals, if present in a limestone, are usually in very small quantity. An aqueous solution of the stone, is prepared by boiling a considerable portion of its powder in water for some time. To this is now added, while hot, Baric Hydrate, BaH_2O_2, in solution, until an alkaline re-action is obtained. The mixture is now filtered. What remains on the filter is thrown away, and to the filtrate, excess of Ammonic Carbonate is added, and the white precipitate of Baric Carbonate is removed by filtration. And the filtrate thus obtained is evaporated to dryness and ignited, until all Ammonic Salts have volatilised. The ignited residue is now treated with a little Alcohol, and the

7. Whether Sodium has been found or not, the residue is dissolved in a little water, and filtered, a little Alcohol and Platinic Tetrachloride added, and the liquid well stirred. A yellow precipitate, even in minute amount, indicates presence of potassium.

B.—*Detection of the Acids.*

1. Carbonic is always the prevailing, and often the only, acid present in Lime and Cement Stones. This acid is usually detected at the outset of the analysis, as already described.

2. Sulphuric Acid may be detected by adding Baric Chloride to a little of the original acid solution of the stone: the occurrence of a white precipitate indicates certainly the presence of Sulphuric Acid.

Hydrochloric Acid. To detect this acid, some of the powdered stone should be dissolved in dilute Nitric Acid: this solution, after filtration, has added to it a few drops of solution of Argentic Nitrate: a white precipitate occurring almost certainly indicates the existence of Hydrochloric Acid, or in other words, a Chloride.

A process for the quantitative Analysis of a Limestone is given in the Roorkee Treatise on Civil Engineering, pp. 109 to 113. The Author of these "Instructions" can recommend the process there described as capable of giving trustworthy results.

INSTRUCTIONS FOR THE ANALYSIS OF POTABLE WATERS.

SECTION II.

A.—Qualitative Analysis.

1. The process given in II., Section I., may also be applied to the analysis of a water, but the water must be concentrated by evaporation to one-sixth or one-eighth of its bulk before the tests are applied. Nearly all natural waters when boiled for some time, or evaporated, deposit part of their solid constituents, chiefly Calcic and Magnesic Carbonates: the *harder* the water is, the greater will be this deposit. For a very careful analysis, it is necessary to determine the constituents in this deposit separately from those which remain in solution. But in many cases these separate determinations may be dispensed with, and the following method may be adopted:—The concentrated water has added to it a few drops of Hydrochloric Acid; this will almost always produce effervescence due to the escape of Carbonic Acid. The presence or absence of this acid may thus be settled. The solution which results may now be analysed

2, 3, 4 and 5, of II.A., Section I. The same solution may also be used for the detection of Sulphuric Acid.

2. For the detection of Potassium and Sodium, paras. 6 and 7 of II.A., Section I., may be adhered to; only the Baric Hydrate should be added to the concentrated water without the previous addition of Hydrochloric Acid.

3. For the detection of Hydrochloric Acid or Chlorides, some of the concentrated water should be acidified by Nitric Acid, and then the Argentic Nitrate added as directed in II.B., Section I., para. 2.

*B.—*Quantitative Analysis.*

The essential points in this are the determination of *a*, Total Solid Matter; *b*, Chlorine; *c*, Organic Matter; and *d*, Hardness.

a, *Total Solids.* 70 cubic centimetres of the water are evaporated at a heat not exceeding 100° C. A Platinum Crucible, with a lid, must be used for this; the lid, of course, being removed during evaporation. When the water residue is quite dry, the lid of the crucible should be put on and the whole weighed. It should be again exposed to heat, and again weighed; if no difference exists between the first and second weighing, the residue is held to be quite dry, but if a difference is observed, the drying by heat

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* The process here given is abbreviated from Wanklyn's and Chapman's Water Analysis, 5th Ed., London, 1879.

must be continued until two successive weighings are the same. The weight of the crucible when clean and dry should be previously ascertained, and this deducted from the aggregate weight of crucible and residue, will, of course, give the amount of Total Solids contained in the water.

Every milligramme of residue corresponds to one grain of solids *per* gallon of water.

b, Chlorine. A standard solution of Argentic Nitrate must be prepared by dissolving 4·79 grammes of pure Argentic Nitrate in one litre of pure water. Every c. c. of this solution precipitates one milligramme of Chlorine.

The process is done thus:—70 c. c. of the water are taken, and a few drops of Neutral Potassic Chromate are added to it: this gives to the water a slightly yellow colour. The standard solution of Argentic Nitrate is now dropped in, from a burette, until the water acquires a permanent brown red colour; the amount of Argentic Nitrate Solution dropped in, is now read off. The number of c. c. used shows the number of grains of Chlorine *per* gallon of water.

If the amount of Chlorine in a water is very small, it may be necessary to concentrate 140 c. c., or even 210 c. c. down to 70 c. c. The amount of solution of Argentic Nitrate used, must be divided by 2, if 140 were used, or by 3, if 210 were used, in order c, *Organic Matter.* Nearly all natural water contains Organic Matter; sometimes it is quite harmless, at other times it is of a dangerous kind. In every case the less Organic Matter a water contains, the better it is for drinking. As a very small amount of some kinds of Organic substances, such as excrementitious matter and the like, in a drinking water is believed to be dangerous, it is necessary that the process for estimating this constituent, should be capable of discriminating between the fractional parts of one-millionth part of the water. The process of Wanklyn and Chapman will do this: It is founded on the fact, that water when boiled with Soda or Potass, or their Carbonates gives off, and that very quickly, any Ammonia it may contain. If Ammonia is in a water it may almost certainly be put down to the existence either now, or previously, of one or more of the dangerous kinds of Organic Matter. The process is further founded on the fact, that all Nitrogerous Organic Matter in solution, (all the dangenous kinds of Organic Matter are Nitrogenous,) when boiled with a strongly Alkaline Solution of Potassic Permanganate are thereby converted into Ammonia, and the Ammonia so produced will also quickly escape from the water on boiling, so that if distilled, the first portions of the distillate contains the whole of the Organic Matter in the form of Ammonia.

The process requires a small metal or glass still;

several straight graduated tubes, and pipettes; a Standard Solution of Ammonia; a Saturated Solution of Sodic Carbonate. Nessler's Solution; the preparation of which has already been described (*vide* Nessler Test, page 4); and, lastly, an Alkaline Solution Potassic-Permanganate, made by dissolving 200 grammes of Caustic Potass and 8 grammes of crystallised Potassic Permanganate in a litre of water. This solution should be boiled for some time, and the loss by evaporation again made up by the addition of pure water.

The process is thus conducted:—One quarter or 250 c. c. litre of water is put in the still and 5 c. c. of the saturated Solution of Sodic Carbonate added. The water is now distilled until 25 c. c. have come over. To this distillate, 1 c c. of the Nessler Solution is added, and its colour compared with 25 c. c. of the Standard Ammonic Solution so diluted, that it may contain about ·001 of a milligramme of Ammonia in each c. c. If this latter shows on addition of 1 c. c. of Nessler Solution, a deeper colour than the water distillate, then the latter contains less Ammonia than ·001 in each c. c. of it. Another Ammonic Solution must now be made so diluted, that each c. c. only contains ·0005 of a milligramme of Ammonia. If this, when Nesslerised as before, gives the same tint as the water distillate, then the amounts of Ammonia in these will be the same. It will be seen from this that the use of the Standard Ammonic Solution is to [illegible] several

Solutions, one of which when Nesslerised, will give colour identical with that yielded by the water distillate.

In this way the amount of Free Ammonia is estimated. All the Free Ammonia has escaped from th water when 75 c. c. have been distilled : indeed i has been found that the first 25 c. c. of the distillat contain three-fourths of all the Ammonia. It is onl therefore, necessary to Nesslerise the first 25 c. c., an one-third of the Ammonia thus found, is added, an the Total Free Ammonia is thus obtained. For instance, if in the first 25 c. c. were found ·0004 of Ammonia in each c. c., the Total Ammonia would b $\cdot0004 \times 25 = \cdot01 + \frac{1}{3} = \cdot013$. And as quarter of litre of water was used, this last number is multiplie by 4, giving ·052 of a milligramme, as the total Fre Ammonia in one litre of the water under examination

The first 75 c. c. of the distillate contains all th Free Ammonia: the residual 175 c. c. yet in th still, contains all the other Nitrogenous Matter. Thi has now to be converted into Ammonia, called for distinction, *Albumenoid* Ammonia. For this purpose 2 c. c. of the Alkaline Permanganate Solution is added The distillation is now recommenced, and each 2 c. c. as it comes over, is Nesslerised as before, an compared with several Standard Solutions of Ammonia and from among these one will be found, when Nesslerised, to have a tint identical with that of the wate

distillate. From this the amount of Ammonia, in the 25 c. c. of distillate may be inferred. The process is repeated with the second 25 c. c. of distillate, and so on. It has been found that all the Ammonia is distilled over, when 75 c. c. of distillate have been obtained. All the amounts of Ammonia are now added together. The calculation is thus done :—Suppose first 25 c. c. gave ·0007 of a milligramme in each c. c., then ·0007 × 25 = ·0175: if the second gave ·0002, then ·0002 × 25 = ·005: and the third gave ·0001, then ·0001 × 25 = ·0025. These together will be ·025, and this number multiplied by 4 gives ·10 as the total Albumenoid Ammonia in one litre of the water under examination. The determination of the Organic Matter in the supposed case, gives Free Ammonia ·054 and Albumenoid Ammonia ·10 parts in one million of water. Small as these quantities appear to be, yet such a water is below the standard of purity, which a potable water should have, the Albumenoid Ammonia in which should not exceed ·07 parts in one million.

d, Hardness.—The harder a water is, it contains the more calcic or lime salts, and it is the more disadvantageous for use in steam boilers, and it also takes more soap to form a lather with it. This last circumstance is the foundation of Clark's Soap Test. A Standard Solution of Soap, is prepared by dissolving 10 grammes of Castille Soap in one litre of Proof

Spirit, (*i.e.*, a mixture of 60 parts Spirit of Wine and 40 parts of water). One c. c. of this solution will precipitate one milligramme of Calcic Carbonate. The Soap Solution usually requires to be adjusted with a Standard Hard Water, made for the purpose, before it is fit for use.

The process for estimating the hardness is thus conducted :—70 c. c. of the water are put into a clean, well-stoppered bottle, and the Soap Solution is cautiously run in from a burette; after each addition of 2 c. c., the bottle is vigorously shaken. When lasting lather appears to be forming, then the Soap Solution is added more cautiously = 0·5 of a c. c. at time. A point will thus be easily reached when t lather becomes permanent for 5 minutes, even when the bottle is laid on its side. The number of c. c. Soap Solution used is now noted, and one c. c. deducted on account of the 70 c. c. of water, as the amount of water will of itself consume a little of t soap. Thus, if the total soap used is 10 c. c., the hardness due to the lime salts is equal to 9 c. c., and such a water is reckoned as of 9 degrees of hardness, or equal to 9 grains of lime salts per gallon, or it expresses the number of grains of Calcic Carbonate, or equivalent Calcic Salts, contained in one gallon of water. This number is often called the Degree of Hardness. Thus a water containing 9 grains of Calcic Carbonate is said to be of 9 degrees of hardness.